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A THERMOANALYTICAL STUDY OF THE SOLID STATE REACTIONS IN THE K_2CO_3–M_xO_y SYSTEMS

Evidence for a kinetic compensation effect

S. Milić[1], *N. Colović*[1], *M. Antonijević*[1] *and F. Gaál*[2]*

[1]Technical Faculty Bor, University of Belgrade, P.O. Box 50, 19210 Bor
[2]Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Yugoslavia

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Abstract

This paper presents the results obtained in the investigation of the reactions of potassium carbonate with some transition metals oxides (TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3). The reactions were carried out under non-isothermal conditions, and thermogravimetric analysis was used to monitor the transformation degree α. Experimental data indicated that the reaction of potassium carbonate and iron(III) oxide occurs in one stage, whereas the reactions of the oxides of titanium, vanadium, chromium and manganese are more complex, involving two-stage processes. Activation energies and pre-exponential factors were determined for all the processes taking place in the investigated systems. For the second stage of the reaction of K_2CO_3 with Cr_2O_3, and V_2O_5 the obtained values of activation energy were 59.2 and 512 kJ mol^{-1} respectively. Based on the values of activation energy and pre-exponential factor, the existence of a kinetic compensation effect was postulated for the three homologous series of reactions.

Keywords: kinetic compensation effect, non-isothermal, potassium carbonate, solid state reactions, transition metals oxides

Introduction

Reactions of the synthesis of inorganic materials based on transition metals oxides and carbonates or oxides of other metals, occurring at higher temperatures, are very complex [1–3], but also very interesting from both the theoretical and practical point of view [4].

The reactions of alkaline carbonates with transition metals oxides yield products with specific characteristics [5]: titanates, vanadates, chromates, manganates, and ferrites. These reactions can be controlled either by diffusion [6] or chemically [7].

Iron oxide, Fe_2O_3, is reactive at elevated temperatures. Its reactions with NiO [8], MgO [1], Li_2CO_3 [2], Na_2CO_3 [7] etc. were investigated. In the reactions of Cr_2O_3 with carbonates [9], and some other oxides (CdO, CuO, MgO, NiO, ZnO), MCr_2O_4 occurs as an intermediate. The rate-determining steps are diffusion of Cr^{3+} through the layer of

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* Author to whom all correspondece should be addressed.

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products and oxygen transport. Titanium(IV) oxide reacts with oxides or carbonates at higher temperatures and forms titanates. It was found that the reaction with barium carbonate in the presence of carbon dioxide yields $BaTiO_3$, whereas the removal of CO_2 from the system results in Ba_2TiO_4 [10, 11]. Manganese(IV) oxide decomposes at higher temperatures, giving a whole range of oxides [12], the reactions being under chemical control.

A kinetic compensation effect has been noticed during the study of the kinetics of catalytic reactions [13–18], as well as in other heterogeneous reactions [19, 20], and lately in the reactions proceeding under non-isothermal conditions [21, 22]. Many authors have attempted to explain the compensation parameter, but no satisfactory explanation has been given yet [23–27]. The existence of this effect was observed in the present study of the kinetics of the reaction of potassium carbonate with a series of oxides of transition metals (TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3) taking place under non-isothermal conditions.

Experimental

All the reagents were of analytical reagent purity.

Initial components were K_2CO_3, TiO_2, V_2O_5, Cr_2O_3, MnO_2, and Fe_2O_3. Mass change in the course of reaction was monitored on a Netzsch, Model 409 thermoscale and the samples were analyzed by X-ray analysis.

Working procedure was the same in all experiments. First, the reacting components (potassium carbonate+oxide) were mixed in an equimolar ratio and homogenized. Afterwards, samples of the same mass (0.750 g) were taken and subjected to heating. All reactions were investigated at various heating rates of 2, 5, 10 and 20 K min^{-1}, in a static air atmosphere. Kinetic curves, $\alpha=f(T)$ or $\alpha=f(t)$, at different linear heating rates were graphically differentiated, which produced kinetic curves representing the dependence of the reaction rate on temperature or time, ($d\alpha/dT$ or $d\alpha/dt$). These curves were used to determine the maximal reaction rate (v_{max}), corresponding temperature (T_m), and the duration of the treatment (t_m).

Results and discussion

Kinetic curves obtained for the reactions of potassium carbonate and transition metals oxides (TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3) were analyzed using the following equations [7, 28]:

$$\frac{d\ln v_{max}}{d(1/T_m)}=-\frac{E}{R} \tag{1}$$

and

$$\frac{d\ln t_m}{d(1/T_m)}=\frac{E}{R} \tag{2}$$

where:

v_{max} – maximal rate of the chemical reaction (determined from the first derivative of the curve $\alpha=f(T)$ or $\alpha=f(t)$),

T_m – temperature corresponding to the maximal rate of the chemical reaction,

t_m – time elapsed to the moment of reaching v_{max}

and using the Ozawa equation [29, 30]:

$$\frac{\mathrm{d}\ln q}{\mathrm{d}(1/T_m)}=-\frac{E}{R} \tag{3}$$

where:

q – linear heating rate.

Chemical reactions between potassium carbonate and oxides of transition metals (TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3) can be represented by the following equations:

$$K_2CO_3+TiO_2=K_2TiO_3+CO_2 \tag{4}$$

$$K_2CO_3+V_2O_5=2KVO_3+CO_2 \tag{5}$$

$$K_2CO_3+0.5Cr_2O_3+0.75O_2=K_2CrO_4+CO_2 \tag{6}$$

$$K_2CO_3+MnO_2=K_2MnO_3+CO_2 \tag{7}$$

$$K_2CO_3+Fe_2O_3=2KFeO_2+CO_2 \tag{8}$$

A common characteristic of all the reactions is the evolvement of carbon dioxide and formation of the corresponding salts: titanates, vanadates, chromates, manganates and ferrites.

In Fig. 1 the diffractogram of the products of the reaction of K_2CO_3 and V_2O_5 is presented, showing that the reaction product is KVO_3.

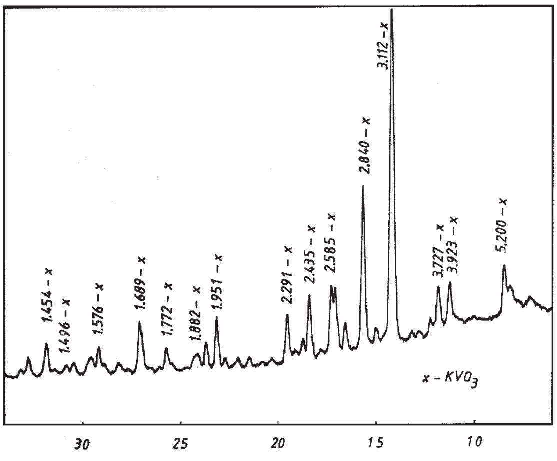

Fig. 1 X-ray diffractogram of the products of reaction (5)

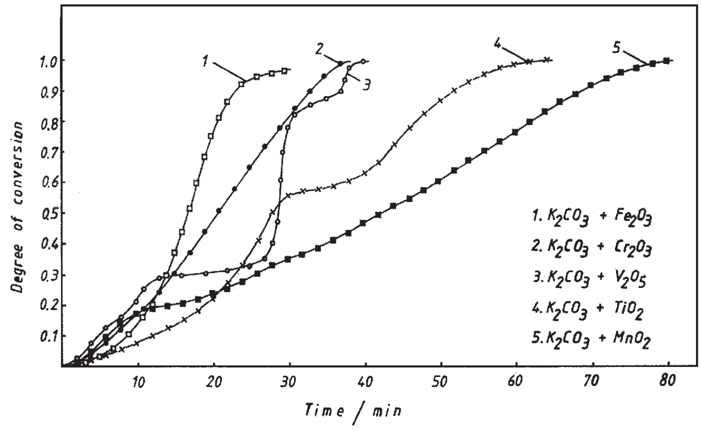

Fig. 2 Kinetic curves obtained for the reaction of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3 (heating rate: 10 K min^{-1})

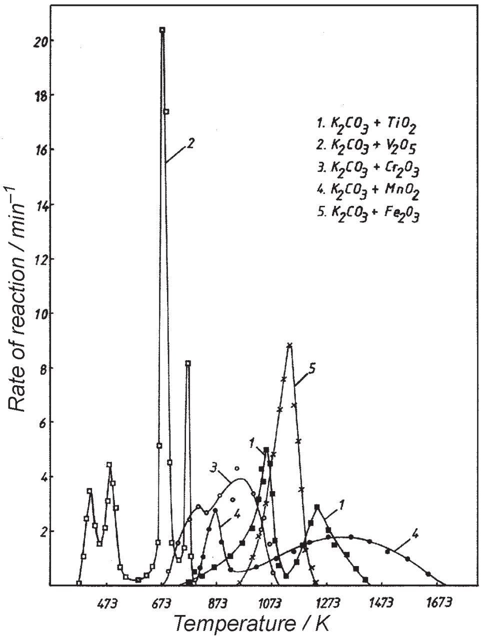

Fig. 3 Dependence of the transformation rate on temperature for the reaction of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2, Fe_2O_3 (heating rate: 10 K min^{-1})

Kinetic curves ($\alpha=f(T_m)$ and $\alpha=f(t_m)$) for all the investigated reactions are of a similar character, which is evident from Fig. 2, showing the dependence of the conversion degree (α) is plotted against the reaction time at a heating rate of 10 K min^{-1}. Graphical derivation of these curves allowed the determination of the maximal reaction rate (v_{max}) and the corresponding time (t_m). The temperature corresponding to the maximal reaction rate (T_m) is determined using the differential form of the kinetic curve $d\alpha/dT$, Fig. 3.

Table 1 presents the values of activation energy (E) and pre-exponential factor (A) obtained for the different heating rates, using Eqs (1) and (2), which can be presented in an expanded form as:

$$\ln v_{max} = \ln A - \frac{E}{RT} \tag{9}$$

$$\ln t_m = \ln A + \frac{E}{RT} \tag{10}$$

Table 1 Values of activation energy and pre-exponential factor for the reaction of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2 and Fe_2O_3

Reaction	Eq. (1)		Eq. (2)		Eq. (3)
	E/ kJ mol^{-1}	A/ min^{-1}	E/ kJ mol^{-1}	A/ min^{-1}	E/ kJ mol^{-1}
1. K_2CO_3+Cr_2O_3 – stage II	59.2	$1.28\cdot10^{2}$	74.6	$4.30\cdot10^{2}$	70.0
2. K_2CO_3+Cr_2O_3 – stage I	69.8	$7.48\cdot10^{2}$	77.0	$1.72\cdot10^{3}$	70.0
3. K_2CO_3+Fe_2O_3 – direct	186.1	$1.67\cdot10^{7}$	182.5	$1.22\cdot10^{7}$	182.2
4. K_2CO_3+TiO_2 – stage I	196.5	$2.49\cdot10^{8}$	227.4	$4.17\cdot10^{10}$	216.0
5. K_2CO_3+TiO_2 – stage II	209.5	$1.90\cdot10^{7}$	230.0	$9.40\cdot10^{7}$	232.0
6. K_2CO_3+MnO_2 – stage I	371.8	$1.04\cdot10^{21}$	379.1	$1.84\cdot10^{21}$	374.2
7. K_2CO_3+V_2O_5 – stage I	381.1	$1.24\cdot10^{28}$	448.0	$1.06\cdot10^{33}$	443.0
8. K_2CO_3+MnO_2 – stage II	400.6	$3.83\cdot10^{13}$	442.2	$6.31\cdot10^{14}$	380.0
9. K_2CO_3+V_2O_5 – stage II	512.0	$2.04\cdot10^{32}$	637.5	$2.63\cdot10^{40}$	615.0

As can be seen from Figs 2 and 3 the investigated reactions do not include dehydration, except for the reaction involving vanadium(V) oxide.

Figure 3 shows that the reaction of K_2CO_3 with iron oxide proceeds in one stage, with v_{max}=8.8 min^{-1}. The temperature (T_m) that corresponds to this rate is 1143 K, which is lower than the decomposition temperature of K_2CO_3 (1164 K) indicating that a direct interaction takes place between the carbonate and oxide (reaction 8).

On the kinetic curve for the K_2CO_3–V_2O_5 system (Fig. 3) there are two peaks with maximal temperatures of 678 and 778 K. The first peak corresponds to the first process, which can be described by Eq. (5). In the temperature range around the first peak (678 K) a direct reaction of K_2CO_3 and V_2O_5 takes place. At higher temperatures (second peak) the reaction mechanism changes, so that the investigated reaction most probably occurs as follows:

a) decomposition of potassium carbonate:

$$K_2CO_3 = K_2O + CO_2 \tag{11}$$

b) reaction between K_2O and V_2O_5:

$$K_2O+V_2O_5=2KVO_3 \tag{12}$$

The decomposition temperature of potassium carbonate decreases in the presence of oxide, so it can be assumed that this reaction mechanism is correct.

The differential kinetic curves for the systems K_2CO_3–Cr_2O_3, K_2CO_3–TiO_2 and K_2CO_3–MnO_2 have two peaks (Fig. 3). The first peaks in all three cases like for the K_2CO_3–V_2O_5 system, correspond most probably to a direct interaction between K_2CO_3 and the corresponding oxide (according to Eqs 4, 6 and 7 respectively), and represent the first process. The temperatures (T_m) corresponding to the maximal rates of the first processes for the K_2CO_3–Cr_2O_3, K_2CO_3–TiO_2 and K_2CO_3–MnO_2 system (813, 1033 and 848 K, respectively) are lower than the dissociation temperature of K_2CO_3.

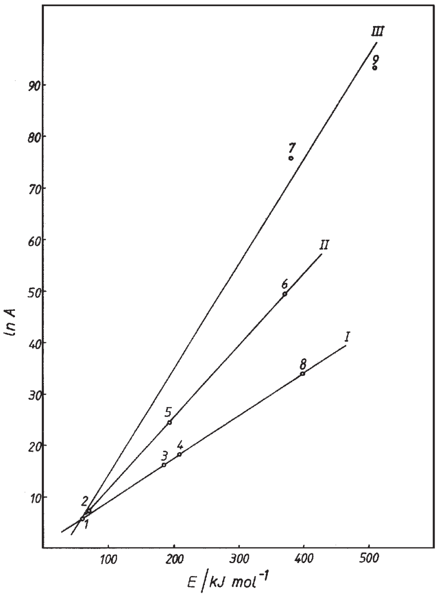

Fig. 4 Kinetic compensation effect for reactions of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2 and Fe_2O_3

The second processes can be explained in a similar way, as in case of the reaction of potassium carbonate and vanadium oxide. In all probability, there is a decomposition of potassium carbonate to K_2O and CO_2 (Eq. 11), followed by the reaction of K_2O and the corresponding oxide:

$$K_2O+0.5Cr_2O_3+0.75O_2=K_2CrO_4 \tag{13}$$

$$K_2O+TiO_2=K_2TiO_3 \tag{14}$$

$$K_2O+MnO_2=K_2MnO_3 \qquad (15)$$

The experiments showed that the products K_2MnO_3 and K_2TiO_3 appear in a molten state, which means that the reactions of K_2CO_3 with MnO_2 and TiO_2 include melting, most probably, of the products, K_2MnO_3 and K_2TiO_3.

As can be seen from Table 1, the values of activation energy and pre-exponential factor of the investigated chemical reactions are relatively high, and the obtained kinetic curves ($\alpha=f(t)$ and $\alpha=f(T)$) have a sigmoid shape, which indicates that the investigated reactions of K_2CO_3 with the investigated oxides are chemically controlled.

By the graphic presentation of $\ln A=f(E)$, the existence of a kinetic compensation effect can be demonstrated for the reactions under study (Fig. 4), which can be written in the following form:

$$\ln A=a+bE \qquad (16)$$

where a and b are the compensation constants.

The three straight lines in Fig. 4 indicate that there are three homologous series of reactions. The points enumerated from 1 to 9 represent the corresponding reactions and stages presented in Table 1. Compensation constants were calculated using regression analysis, and their values are: for curve I, $a=1$ and $b=0.083$; for curve II, $a=-2.2$ and $b=0.137$; and for curve III, $a=-6$ and $b=0.2$.

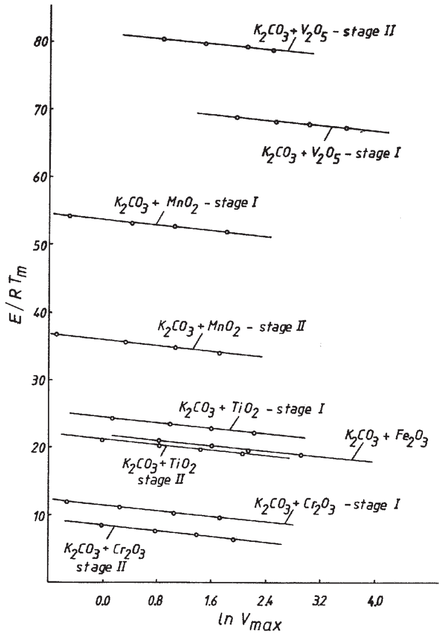

Fig. 5 Dependence of E/RT_m on $\ln v_{max}$ for the reactions of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2 and Fe_2O_3

Experimentally established order of decrease in reactivity for the reactions of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2 and Fe_2O_3, based on Fig. 4 is:

Curve I:

1. K_2CO_3+Cr_2O_3 – stage I
2. K_2CO_3+Fe_2O_3 – direct
3. K_2CO_3+TiO_2 – stage II
4. K_2CO_3+MnO_2 – stage II

Curve II:

1. K_2CO_3+Cr_2O_3 – stage I
2. K_2CO_3+TiO_2 – stage I
3. K_2CO_3+MnO_2 – stage I

Curve III:

1. K_2CO_3+Cr_2O_3 – stage II
2. K_2CO_3+Cr_2O_3 – stage I
3. K_2CO_3+V_2O_5 – stage I
4. K_2CO_3+V_2O_5 – stage II

It is also evident from Fig. 4 that the most reactive oxide is chromium oxide, while the most inert is vanadium oxide. Those reactions/stages, denoted by points lying on the compensation lines of a smaller slope are more reactive, which means lower values of the compensation parameter *b*. Also, more reactive are the reactions which lie closer to the coordinate origin (in this case, these are the reactions of K_2CrO_4 formation).

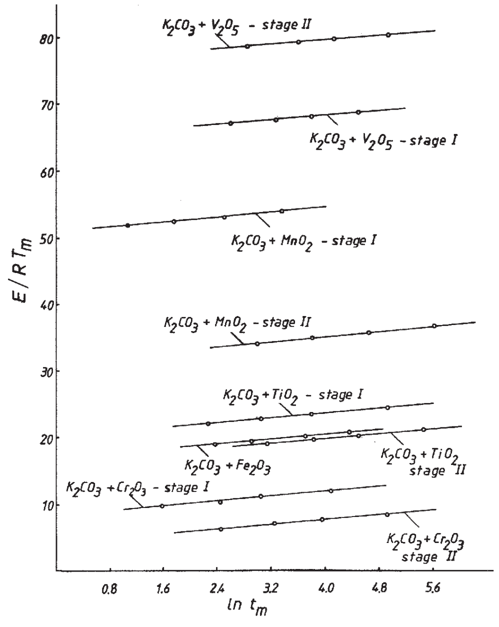

Fig. 6 Dependence of E/RT_m on $\ln t_m$ for the reactions of K_2CO_3 with TiO_2, V_2O_5, Cr_2O_3, MnO_2 and Fe_2O_3

In their previous papers Colović [28, 31] *et al.* have concluded that the reactivity of particular reactions and stages can be compared and presented by plots where x-axis is $\ln t_m$ or $\ln v_{max}$, and y-axis is E/RT_m.

The diagrams in Figs 5 and 6 contain parallel straight lines which correspond to particular reactions and stages of the investigated reactions, allowing their comparison. Lines with the largest value of the term E/RT_m correspond to the most inert reactions. With decrease of the E/RT_m value, reactivity of the investigated reaction increases (from stage II of the reaction K_2CO_3–V_2O_5 to stage II of the reaction K_2CO_3–Cr_2O_3).

Reactivity of the investigated systems in particular stages can be determined from the position of these lines, as they contain relation between v_{max} and t_m, on the one hand and between kinetic parameters (E, A) and the temperature at which reaction takes place, on the other. Numerical values of these parameters are basically related to the nature of the matter that transforms. Because of that, when comparing the dependence of E/RT_m on $\ln v_{max}$ and E/RT_m on $\ln t_m$ for different systems, their reactivities in particular processes/stages are actually compared.

On comparing the diagrams in Figs 5 and 6 with those in Fig. 4 it can be concluded that there is a good agreement of these methods for monitoring the reactivity of the investigated oxides with potassium carbonate.

Conclusions

1. The reaction of K_2CO_3 and Fe_2O_3 is a one-stage reaction, and the value of activation energy for this reaction is 186.1 kJ mol^{-1}.
2. The reactions of K_2CO_3 with the oxides of titanium (TiO_2), vanadium (V_2O_5), chromium (Cr_2O_3) and manganese (MnO_2) are two-stage reactions.
3. The values of activation energy for all the reactions range from 59.2 to 512 kJ mol^{-1}, indicating that the reactions are chemically controlled.
4. Kinetic compensation effect indicates that there are three homologous reaction series for the reaction system K_2CO_3-M_xO_y.
5. Reactivities of the different reactants in particular stages can be estimated from the series of parallel straight lines showing the dependence of E/RT_m on $\ln v_{max}$ and E/RT_m on $\ln t_m$.

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